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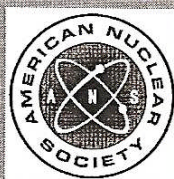
August 4, 2008

ANSI/ANS-16.1-2003 (R2008)

measurement of the leachability
of solidified low-level radioactive
wastes by a short-term
test procedure

an American National Standard

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published by the
American Nuclear Society
555 North Kensington Avenue
La Grange Park, Illinois 60526 USA

ANSI/ANS-16.1-2003

**American National Standard
Measurement of the Leachability
of Solidified Low-Level
Radioactive Wastes by a
Short-Term Test Procedure**

Secretariat
American Nuclear Society

Prepared by the
**American Nuclear Society
Standards Committee
Working Group ANS-16.1**

Published by the
**American Nuclear Society
555 North Kensington Avenue
La Grange Park, Illinois 60526 USA**

Approved July 07, 2003
by the
American National Standards Institute, Inc.

American National Standard

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Foreword

(This Foreword is not part of American National Standard for the Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, ANSI/ANS-16.1-2003.)

The characteristics of radioactive wastes from the nuclear industry are dependent on many diverse factors, most of which do not lend themselves to simple definition and standardization. In this standard, low-level wastes are considered to be those radioactive wastes that are defined as low-level in Title 10, *Code of Federal Regulations*, Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste" (2003). In general, Section 61.2 of Part 61 defines low-level wastes as those containing source, special nuclear, or by-product materials that are not classified as high-level radioactive waste, transuranic waste, spent nuclear fuel, or uranium or thorium tailings and waste. Resistance to leaching of radionuclides is not specifically mentioned in Part 61 nor is containment of radionuclides called out as an express requirement for low-level radioactive waste packages. Minimization of contact of waste by water is a fundamental concern of Part 61, however, as evidenced by the statement in Section 61.7 that "... a cornerstone of the system is stability ... so that ... **access of water to the waste can be minimized**. Migration of radionuclides is thus minimized ..." (bold emphasis added).

In addition, there are several statements in Section 61.57 that address minimization of contact of water with waste. These statements are in recognition of the fact that contact of waste with water is an initial step in a potentially major pathway for radionuclide release and migration off-site. "Leaching," or the release of radionuclides from a waste form through contact with water, is thus a major factor in the subsequent migration of the radionuclides from the waste, through groundwater, and off the site. It follows, therefore, that leaching is a phenomenon that is of fundamental interest in low-level radioactive waste disposal and that the measurement of the leach resistance of potential waste forms is important in low-level waste management.

Low-level radioactive waste accrues in the form of combustible, noncombustible, compactible, and noncompactible solids (cloth, metal, paper, wood), liquids (evaporator bottoms, decontamination solutions), slurries (filter sludges, ion-exchange resins), and powders (incinerator ash, salts). The ANS-16.1 standard was designed principally for one type of low-level radioactive waste: low-level, non-self-heating, radioactive fluids (liquids, slurries, and free-flowing powders). However, it can be used to measure the leach resistance of any waste solidified into a well-defined geometric shape.

An accepted method for managing these liquids, slurries, and powders is solidification, packaging, and subsequent shipment for disposal by shallow-land burial. Solidification can restrict dispersal during handling and transportation and can provide a nonchanging volume during the residence time of the waste in the burial trench.

At present, generators of low-level radioactive wastes (e.g., nuclear power plants, laboratories, and hospitals) need a common basis for evaluating the alternatives for packaging, handling, storing, and shipping their radioactive wastes. Vendors of solidification systems need a common basis for evaluating the leachability of the waste forms made by their solidification processes. Burial ground operators need leaching information to improve the efficiency of their handling, disposal, and site maintenance operations. The 5-day test provides a measure of leach

resistance performance that can be done in the field in a reasonable time period to provide confidence to generators, vendors, and operators that the material intended for shallow burial meets minimum requirements for leach resistance (for example, the U.S. Nuclear Regulatory Commission requires a minimum leachability index of 6.0 for radioisotopes).

Leaching, which can occur when water contacts a solidified waste form, is an important mechanism for the dispersal of radioactivity. Leach testing has thus been recognized as a primary technique for the evaluation and comparison of solidified waste forms.^{1,2)} Even so, the situation remains complex for several reasons:

- (1) leaching can proceed by several concurrent mechanisms such as diffusion, dissolution, and erosion, the relative importance of which can change with time, and temperature, substances dissolved in the water, matrix material, the radionuclides of interest, pH, and other variables;
- (2) the actual leaching conditions that a solidified waste form will encounter during its sound life (i.e., the time during which the waste form meets the specifications for all applicable parameters) are imprecisely known, with postulated conditions varying widely;
- (3) investigators of waste forms have tended to use leach testing procedures unique to their own studies, which makes comparisons difficult.

As a first step toward rectifying the last situation, the International Atomic Energy Agency (IAEA) published a suggested standard leach test in 1971.¹⁾ This suggested test met with consent in principle but was not put into practice. Instead, much of the leach testing being performed used procedures described as "modified" IAEA tests. The "modifications" were unique to individual laboratories, so that standardization and comparability of results was still lacking. The test presented in the ANSI/ANS-16.1-2003 standard has much in common with the original IAEA test.

Working Group ANS-16.1 of the Standards Committee of the American Nuclear Society had the following membership at the time it approved this standard:

R. D. Spence, Chair, *Oak Ridge National Laboratory*

O. U. Anders, *Individual*

H. W. Godbee, *Individual*

A. Icenhour, *Oak Ridge National Laboratory*

R. M. Neilson, *Idaho National Engineering and Environmental Laboratory*

This standard was processed and approved for submittal to ANSI by the American Nuclear Society's Nuclear Facilities Standards Committee (NFSC) on ANSI/ANS-16.1-2003, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure." Committee approval of the standard does not necessarily imply that all committee members voted for its

¹⁾ "Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method," E. D. HESPE, Ed., International Atomic Energy Agency, *At. Energy Rev.*, **9**, 1 (1971).

²⁾ "Long-Term Leach Testing of Solidified Radioactive Waste Forms," ISO 6961-1982(E), International Organization for Standardization.

approval. At the time it approved this standard, the NFSC committee had the following members:

D. J. Spellman, Chair, *Oak Ridge National Laboratory*
S. Ahmad, Standards Administrator, *American Nuclear Society*

C. K. Brown, *Southern Nuclear Operating Company*
R. H. Bryan, Jr., *Tennessee Valley Authority*
H. Chander, *U.S. Department of Energy*
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M. J. Wright, *Entergy Operations*

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Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure

1 Scope, Purpose, and Application

1.1 Scope

This standard, ANSI/ANS-16.1-2003,¹⁾ provides a uniform procedure to measure and index the release of radionuclides from waste forms as a result of leaching in demineralized water for 5 days.²⁾ The results of this procedure do not apply to any specific environmental situation except through correlative studies of actual disposal site conditions. The test presented in this standard has much in common with the original International Atomic Energy Agency proposal and has by now become familiar to those working in the radioactive waste-form development field. It contains the provisions published in the original version of this standard in 1986.

1.2 Purpose

The quantification of the leaching characteristics of solidified wastes requires a standardized, practical method to measure the ability of the solids to impede the release of radioisotopes when water comes into contact with them. The purpose of this standard is to establish such a test, define a material parameter, and provide a mathematical procedure for calculating a "Leachability Index" value for the test data collected over the time period of the test.

This standard is intended to serve as a basis for indexing radionuclide release from solidified low-level radioactive waste forms in a short-term (5-day) test under controlled conditions in a well-defined leachant. It is not intended to serve as a definition of the long-term (several

hundred to thousands of years) leaching behavior of these forms at conditions representing actual disposal conditions.

Under actual leaching conditions, mechanisms other than diffusion (e.g., chemical reaction, surface layers and films, cracking, etc.) are important considerations. Also, the interplay of retardation mechanisms (filtration, ion exchange, coprecipitation, etc.) and enhancement mechanisms (chelation, desorption, dissolution, etc.) for radionuclide migration are important considerations.

1.3 Application

The mechanisms involved in leaching can differ from one type of material to another, from one leachant to another, and from one set of leaching conditions to another. However, if they are known through generic studies, predictions for the release of radioactivity as a function of time can be made. In spite of the differences in materials, leachants, and conditions, a procedure applicable to all products of low-level radioactive waste solidification processes can be devised for purposes of quantitative assessment. The test set forth in this standard is short-term, simple, and emphasizes reproducible conditions that can be readily achieved. The essential test parameters are fixed in detail.

The test consists of a procedure in which the leachant is replaced at designated intervals to generate seven data points over 5 days and ten data points if the test is extended to 90 days. The procedure permits the accumulation of sufficient data in a reasonably short time for quantitative assessment purposes. In its "extended" form, the laboratory leaching can be extended

¹⁾ANSI/ANS-16.1-2003 is hereafter referred to as "this standard."

²⁾Periods of time with the units of days or hours are spelled out since the letters "d" or "h" are used to represent other quantities.

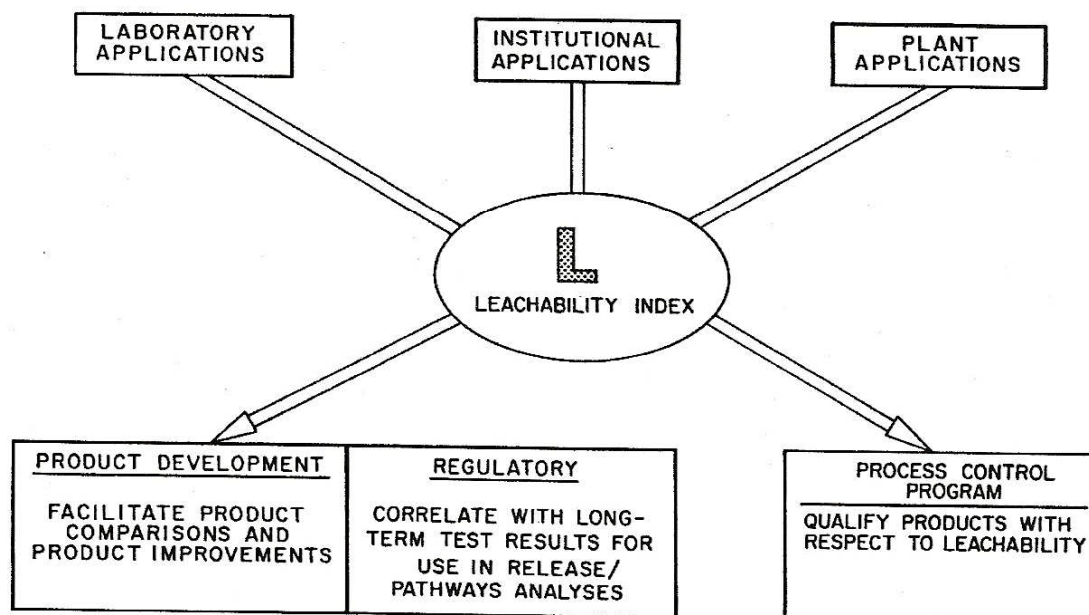


Figure 1.

to 3 months as part of the overall related generic studies.³⁾

The data obtained by the procedure of this standard are expressed as a material parameter of the leachability of each leached species, called the "Leachability Index" (L). Some of the anticipated uses for the Leachability Index are presented in Fig. 1.

2 Glossary of Terms

aliquot: A known fractional part of a defined quantity.

binder: Solidification agent.

cumulative fraction leached: The sum of the fractions leached during all previous leaching intervals, plus the fraction leached during the last leaching interval, using the initial amount of the species of interest present in the specimen as unity (100%) and assuming no radioactive decay.

fraction leached: A portion of a constituent of a specimen or waste form that has been released from the specimen or waste form during the leaching process, using the quantity present initially as unity (100%).

leachability: A rate constant (or a combination of several rate constants) that describes the leaching of a nuclide from a material under a given set of conditions.

Leachability Index: An index value related to the leaching characteristics of solidified waste materials as measured by the leach test defined in this standard. In this standard, the Leachability Index has an exact theoretical meaning only for homogeneous, chemically inert materials, for which bulk diffusion is the predominant rate-determining process during leaching.

leachate: Leachant after use.

leachant: The liquid that contacts the specimen during the course of a leaching test or contacts a solid waste form at a disposal site.

³⁾ See Annexes B and E.

leaching interval: The length of time during which a given volume of leachant is in contact with a specimen or solid waste form.

leaching rate/leach rate: The amount of a constituent of the specimen or solid waste form that is leached during one time unit (e.g., g/day or $\mu\text{Ci/s}$). It is frequently expressed per unit of exposed surface area [e.g., $\text{g cm}^{-2} (\text{day})^{-1}$].

leach test specimen/leach specimen: The solid body that is immersed into the leachant during the leach test. This body must be representative of the solid that is formed by the combination of waste with a solidification agent.

leach test/leaching test: Procedure to be followed for the determination of the Leachability Index.

may: Denotes permission, neither a requirement nor a recommendation.

packaging: Any material or structure covering the surface of a waste such as a plastic bag, drum, concrete cask, etc., but exclusive of a coating or surface treatment.

remaining fraction: Unity minus cumulative fraction leached (i.e., the fraction still remaining with the specimen or waste form after leaching) assuming no decay of the radioactivity.

residual liquid: Free liquid present in the specimen container at the time the specimen is removed from the container.

semi-infinite medium: A body of which the outer boundary is considered to be effectively at an infinite distance from the inner region.

shall: Denotes a requirement.

should: Denotes a recommendation.

wash-off: Liquid containing the mobile surface contamination removed from the specimen by immersing it in demineralized water for 30 s.

3 Test Procedure

Many different testing methods with various leachant compositions, leachant-renewal frequencies, and test conditions (e.g., temperatures and pressures) have been used in the past to determine the amount of a radionuclide leached from a solidified waste form as a function of time⁴⁾ [1–6]⁵⁾. Since these factors interact to influence the leach test results, this standard's test specifies a defined leachant, a set leachant-renewal schedule, a fixed leachant temperature, and other specified test conditions. The procedure can be extended to other leachants⁶⁾ and different leachant-renewal frequencies (as well as other temperatures and test conditions) so that it more nearly represents anticipated conditions under which a solidified waste form may be stored, transported, or disposed⁶⁾ but are not part of this standard.

3.1 Specimen Preparation

The method for preparing proper test specimens is specific for each waste type and solidification process. A specific procedure by which specimens that meet the following specifications can be prepared shall be developed for each given type of solid under consideration.

Precautions shall be taken to ensure that the specimen is representative of the solidified waste (see "Glossary of Terms," Section 2) and that the homogeneity of the test specimen is the same as that of the material in the actual solidified waste form. While a small specimen is desirable to limit the radiation field, it shall not be so small that it compromises the specimen homogeneity, requires unattainable analytical sensitivities, or provides substantial difficulties for specimen preparation. The test specimen shall be prepared in the same or similar manner as that established for the solidification process. If specimens are obtained by core drilling of waste forms (which should be avoided), the procedure shall be described, and the specimen shall have surfaces representative of the actual waste form. Using cast samples rather than samples core drilled from a cast monolith is recommended because the pro-

⁴⁾ See Annex D.

⁵⁾ Numbers in brackets refer to corresponding numbers in Section 4, "References."

⁶⁾ See Annex E.

cess of cutting a sample from a monolith alters the surface of the waste form and may possibly result in microcracks in a sample obtained in this manner. In some cases, core drilling is the only way to accomplish the desired testing, but the possible alterations in the sample matrix structure should be kept in mind.

In addition to being representative of the solidified waste, the specimen shall have a well-defined shape, mass, and volume. The surface condition of the specimen should be representative of the surface condition of the actual full-scale waste product. Where possible, the specimen shall be a monolithic cylinder, parallelepiped, or sphere, the dimensions of which are reported. Cylinders shall have a length-to-diameter ratio in the range of 0.2 to 5. Parallelepipeds shall have a length-to-minimum-thickness ratio in the range of 0.2 to 5. The test specimen geometry should be cylindrical, if possible. The minimum specimen dimension recommended should be 1 cm, unless a need to employ a smaller specimen (e.g., to minimize personnel radiation exposure) is demonstrated.

The representative specimen of the product of a given solidification process shall be prepared, or cast, so that the casting conforms to the sides of the specimen preparation container (to provide a smooth surface), voids within it are eliminated, and homogeneity (as uniform as the character of the material permits) is attained. For glasslike or thermosetting mixtures, this container should be heated to provide a thermal history representative of that which the actual solidified waste form undergoes. The thermal history of the test specimen shall be reported. Immediately after preparation the specimen shall be placed into the specimen container, which may be the same as the specimen preparation container.

The specimen container shall remain sealed during the storage period between preparation and leach testing. The specimen container(s) shall be constructed of material(s) known to be chemically unreactive toward the specimen (e.g., polyethylene, polypropylene, stainless steel, ceramic, and glass). No single container material appears to be superior for all solidified waste products.

3.2 Leach Test Vessel

The vessel in which leaching takes place should be constructed of an "unreactive" material. A material is considered unreactive if

- (1) it does not react chemically with the leachant or the specimen;
- (2) it does not sorb chemical species extracted from the specimen or those in the leachant itself. This requirement applies to the species of interest extracted from the specimen during leaching. It also applies to those major species extracted during leaching, which influence the composition of the leachant. Sorption shall be determined by a blank test run. A leach vessel made of a material that is sorbent toward the extracted species of interest may be used, provided that either the extent of sorption is small (<5% of the incremental fraction leached) or the sorbed species are removed from the container and analyzed at the same frequency as the leachate is sampled and replaced;
- (3) it does not release interfering species that alter the composition of the leachant during the leaching process;
- (4) it can withstand the conditions involved in leaching.

The leach test vessel shall be constructed so that excessive evaporation of the leachant (>2% over 24 hours) is prevented. The dimensions of the vessel shall permit the entire external geometric surface area (>98%) of the immersed specimen to be in contact with the leachant during the entire leaching interval. The dimensions of the leach test vessel shall also be sufficient to hold the leachant while leaving some free volume for convenience in manipulation of both specimen and leachant.

3.3 Leachant

The leachate shall be sampled and entirely replaced at designated time intervals. The leachant shall be demineralized water with an electrical conductivity of <5 $\mu\text{mho/cm}$ at 25°C and a total organic carbon content (TOC) of <3 ppm. The temperature of the leachant shall be maintained between 17.5 and 27.5°C during the test.

3.4 Leach Test Method

After removal from the specimen container and prior to the initiation of the leach test, the test specimen shall be rinsed by immersion in demineralized water for 30 s. The rinse water volume shall be the same as the required leachant volume (described below).

The container used to store the specimen before leaching shall then be rinsed with an amount of water equal to its volume, to recover any radioactivity present in residual liquid or retained on the container walls. This "container rinse" and the specimen rinse water ("wash-off") are then to be combined and analyzed to determine the quantity present of each radionuclide of interest. The latter are expressed as fractions $(a_r/A_o)_i$, defined as the ratio of activity of the radionuclide i that is present in the combined rinse $(a_r)_i$ to the activity of the same radionuclide in the specimen $(A_o)_i$ at the time it is immersed in the first portion of the leachant (i.e., the beginning of the first leaching interval). This fraction shall be reported for each radionuclide of interest. All radioactivities measured shall be recorded for a common reference time, for example, the beginning of the first leaching interval.

The specimen shall be supported in the leachant by any convenient device, made from unreactive material (as defined above), that does not interfere with the leachate removal and replacement; does not impede leaching; does not damage the surface of the specimen; and, as mentioned above, does not preclude more than a small fraction of the specimen's external surface (<2%) from exposure to the leachant. Examples of suitable specimen supports include wires for suspension, rigid support stands, or coarse-weave wire-mesh baskets. The specimen shall be located within the leachant so that it is surrounded on all sides by a leachant layer.

Sufficient leachant shall be used so that the ratio of the leachant volume, V_L , and the specimen external geometric surface area, S , is maintained within fixed bounds during the leaching interval as given by

$$\frac{V_L (\text{cm}^3)}{S (\text{cm}^2)} = 10 \pm 0.2 (\text{cm}) .$$

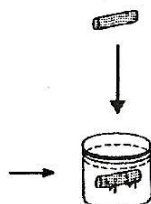
For example, a 1-cm-diameter, 1-cm-long right circular cylinder (surface area 4.71 cm²) would need 47.1 ml of leachant. A ratio of leachant volume to specimen external geometric surface area of 10 cm is usually sufficient to minimize leachant-composition changes during reasonably short leaching intervals, while providing a sufficient concentration of extracted species for analysis. In cases where the minimum leachant layer requirement and the leachant volume to specimen surface area ratio requirement cannot be met concurrently, the latter requirement takes precedence, and all specimen surfaces shall be as uniformly covered with leachant as practicality permits. The leachant shall not be stirred during the leaching interval.

At the end of each leaching interval, the leachate shall be removed from the specimen. Quickly removing the specimen from the used leachant and placing it into fresh leachant in a new leach test vessel is an acceptable and widely employed procedure. After leachate removal, the leach test vessel shall be rinsed with demineralized water to remove residual leachate and contained radioactivity. The specimen may also be momentarily rinsed (<5 s) in demineralized water after leachate removal but before leachant renewal. The radioactivity in these rinses shall be measured and included with that of the leachate just removed. During leachant renewal the specimen should be exposed to the air for as short a time as reasonably achievable. In no case shall its surface be allowed to dry completely. The specimen shall then be contacted with fresh leachant solution for the specified time of the next leaching interval.

The rate of radioactivity release, and hence the calculated Leachability Index value, can be a function of the leachant-renewal frequency. A standardized uniform leachant-renewal schedule is thus required. The leachate shall be sampled, and the leachate completely replaced after cumulative leach times of 2, 7, and 24 hours from the initiation of the test, as illustrated in Fig. 2. Subsequent leachate sampling and leachant replacements shall be made at 24-hour intervals for the next 4 days, for a total of 5 days for the standard test. In the "extended" option, three additional leach intervals of 14, 28, and 43 days each extend the entire test to 90 (5 + 14 + 28 + 43) days, as illustrated in Fig. 2. As noted on Fig. 2, the leachant change for the optional last three renewal periods of the test may

SPECIMEN (CUBE, CYLINDER, OR SPHERE) OF SOLIDIFIED NUCLEAR WASTE (ACTUAL OR SIMULATED)

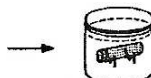
DEMINERALIZED WATER (VOLUME OF WATER + SURFACE AREA OF SPECIMEN = 10 ± 0.2 cm)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

$$\begin{aligned}\Delta t &= 2 \text{ hours} \\ t &= 2 \text{ hours} = 7.2 \times 10^3 \text{ s} \\ T &= 1.8 \times 10^3 \text{ s [see Eq. (1)]}\end{aligned}$$

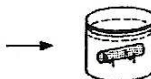
REPLACE LEACHATE WITH FRESH LEACHANT (DEMINERALIZED WATER)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

$$\begin{aligned}\Delta t &= 5 \text{ hours} \\ t &= 7 \text{ hours} = 2.52 \times 10^4 \text{ s} \\ T &= 1.48 \times 10^4 \text{ s}\end{aligned}$$

REPLACE LEACHATE WITH FRESH LEACHANT (DEMINERALIZED WATER)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

$$\begin{aligned}\Delta t &= 17 \text{ hours} \\ t &= 24 \text{ hours} = 8.64 \times 10^4 \text{ s} \\ T &= 5.12 \times 10^4 \text{ s}\end{aligned}$$

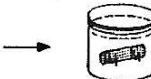
REPLACE LEACHATE WITH FRESH LEACHANT (DEMINERALIZED WATER)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

$$\begin{aligned}\Delta t &= 24 \text{ hours} \\ t &= 48 \text{ hours} = 1.73 \times 10^5 \text{ s} \\ T &= 1.26 \times 10^5 \text{ s}\end{aligned}$$

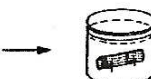
REPLACE LEACHATE WITH FRESH LEACHANT (DEMINERALIZED WATER)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

$$\begin{aligned}\Delta t &= 24 \text{ hours} \\ t &= 72 \text{ hours} = 2.59 \times 10^5 \text{ s} \\ T &= 2.14 \times 10^5 \text{ s}\end{aligned}$$

REPLACE LEACHATE WITH FRESH LEACHANT (DEMINERALIZED WATER)



ANALYZE REMOVED LEACHATE FOR ELEMENTS a_1, a_2, \dots

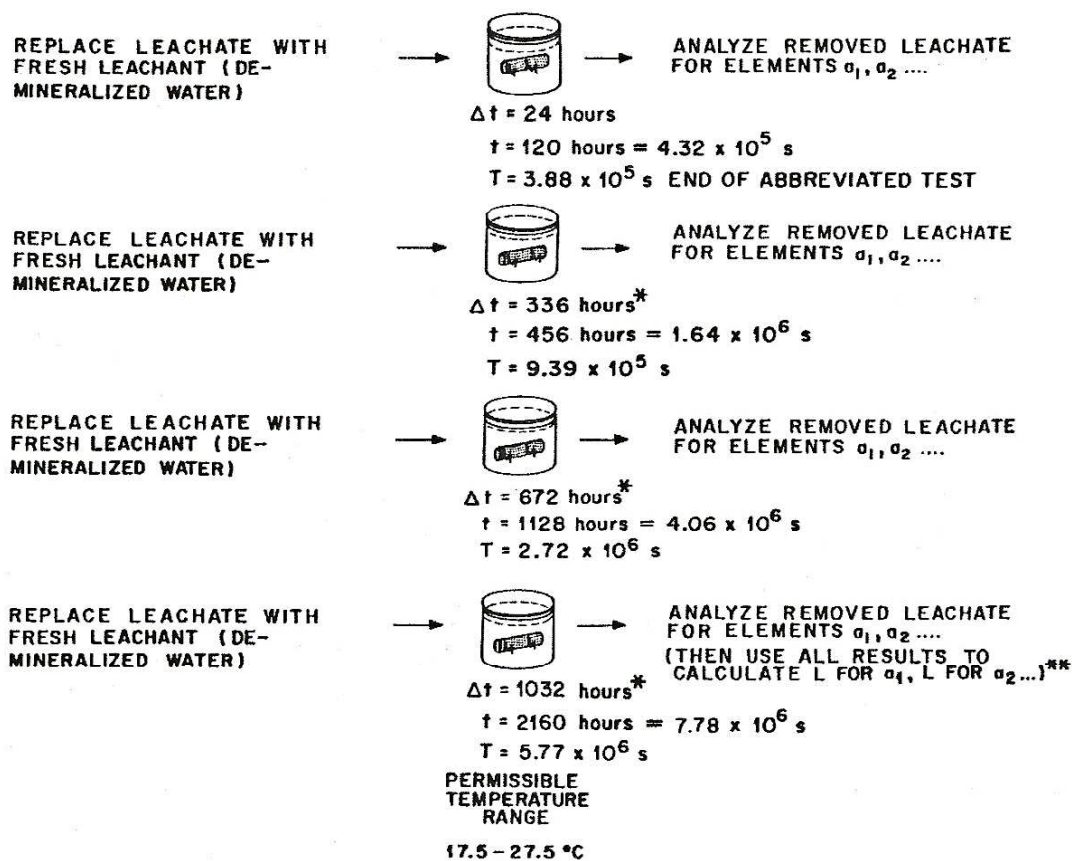
$$\begin{aligned}\Delta t &= 24 \text{ hours} \\ t &= 96 \text{ hours} = 3.46 \times 10^5 \text{ s} \\ T &= 3.01 \times 10^5 \text{ s}\end{aligned}$$

Figure 2.—Continues on next page.

be shifted by 1 day. This permits a leachant change scheduled on Saturday (or Sunday) to be shifted to Friday (or Monday) for these last three optional renewal periods. The reasoning behind

this is that with the protracted leachant renewal periods, the boundary conditions of the model⁷⁾ are not satisfied and a day under or a day over will not make any significant differ-

⁷ See Annex B.



*THE LONGER LEACHING INTERVALS OF 2, 4, AND 6 WEEKS MAY VARY BY ± 1 DAY.

**L = LEACHABILITY INDEX. A HIGH L FOR a_1 INDICATES GOOD RESISTANCE TO LEACHING OF ELEMENT a_1 .

Figure 2.—Continued.

ence in the results after such extended time periods. This standard requires that the leachant changeout time be short and insignificant relative to the duration of a leaching interval.

For purposes of extended leaching times or evaluating the effects of longer immersions, a longer-time "extended test" is defined by the same sequence, but with the three additional longer leaching intervals. This extended test requires 90 days of testing.

3.5 Leachate Analysis

An aliquot of the leachate shall be taken at the end of each leaching interval to determine, by

a suitable method, the amounts $(a_n)_i$ of the species of interest present in the leachate volume. Any generally accepted state-of-the-art analytical procedure may be employed. The release of the species of interest will always be determined by measuring the quantity present in the leachate rather than the residual in the specimen.

Leachate aliquots taken for analysis shall be representative of the leachate from which they are taken. The intent is to provide aliquots that will permit a determination of all the radioactivity that has been removed from the test

specimen during the leaching interval. This includes any radioactivity associated with particulate solids in the leachate. Stirring of the leachate to suspend particulate solids prior to taking the leachate aliquot or dissolution of such solids by the addition of chemicals to the leachate before sampling may be performed, if standard. If precipitation occurs in the leachant during the leaching interval, the amount of the extracted species of interest associated with the precipitate shall be determined and added to the amount of the dissolved species. Under no circumstances shall the leachate be filtered and the filter media with the residue be discarded without analysis.

4 Presentation and Analysis of Data

The following experimental information⁸⁾ shall be recorded:

- (1) the type of waste and the proportion (by weight and volume) of waste and binder incorporated into the waste-binder mixture prior to solidification;
- (2) the type and composition of the immobilizing material (binder), including additives. Commercial names shall be used;
- (3) the radionuclides and/or the nonradioactive tracers and the total amount of each in the leaching specimen both as prepared (A_p)_i and after the 30-s rinse (A_o)_i.

In the following description, the subscripts, *i*, are omitted to simplify the presentation. The value of A_o can be obtained by subtracting the contaminant present in the combined initial rinse (a_r) described in 2.4, from that in the specimen as prepared (namely, $A_o = A_p - a_r$). The values of A_p and a_r are corrected for radioactive decay and reported as of a reference time (e.g., the time representing the first exposure of the specimen to the leachant, namely, the beginning of the first leaching interval). The amount of contamination (radionuclide or stable nuclide) may be reported in units of microcuries (μCi) or dis-

integrations per second (Bq) or mass [e.g., micrograms (μg)]. It may also be reported as a fraction of the quantity in a reference source of the same contaminant;

- (4) any departures from the specified methods of specimen preparation;
- (5) shape, mass, and dimensions of the leach test specimen;
- (6) the history of the specimen between preparation and leaching, including time and temperature, as well as any other relevant information;
- (7) beginning and end of each leaching interval (i.e., date, hour, and minute);
- (8) electrical conductivity of leachant ($\mu\text{mho}/\text{cm}$ at 25°C) and total organic carbon;
- (9) volume of leachant used during each leaching interval;
- (10) temperature of the leachate at the end of each leaching interval;
- (11) volume of leachate aliquot used for analysis;
- (12) type and amount of contaminant present in the leachate aliquots at the end of each leaching interval. The amount may be reported in units of microcuries (μCi) or disintegrations per second (Bq) or mass (μg). If the half-life of a radionuclide of concern does not exceed the time elapsed since the beginning of the test by a factor of 20, the data shall be corrected for radioactive decay to the reference time. Although any convenient time may be used as the reference time, the time of the beginning of the first leaching interval (see 4.2) should be used.

The amount of a radionuclide or nonradio-nuclide should be reported as the fraction of the radioactivity or mass of a reference source of the same radionuclide or nonradionuclide. If this method is chosen, all measurements of a given nuclide shall be reported relative to the same reference source. If the leach test is performed with nonradioactive tracers, the analytical method used shall be sensitive enough to provide meaningful data.

⁸⁾ This information is recorded in Parts A, B, and C of forms such as those illustrated in Annex A.

In this case, A_o represents the total amount of tracer present in the specimen after the initial rinse, and the leaching data (a_n , etc.) are presented in units of micrograms (μg) or some other parameter specific for the analytical procedure. Whichever way is chosen, the units shall be consistent;

(13) surface appearance of specimen before and after leaching;

(14) observed changes in shape and dimensions of specimen during test;

(15) whether the leachate contained undissolved solids.

4.1 Presentation of Test Data

The results of the combined rinse-water determination are entered as "Experimental Data." If the relative amount of radioactivity is significantly greater than that obtained in previous generic studies or significantly exceeds the specifications for the waste form, the leach test shall be terminated, the reasons for the discrepancy ascertained, and the test repeated. Significant discrepancies from previous generic testing or from specifications can indicate inadequate performance of leach testing procedures, a nonrepresentative specimen, a waste form that was not properly prepared, and other less obvious reasons. If no significant discrepancies exist, the collection of data shall continue through the stated testing period.

The incremental fraction leached (a_n/A_o), the incremental leaching rate $[(a_n/A_o)/(\Delta t)_n]$, and the cumulative fraction leached ($\sum a_n/A_o$) shall be recorded as functions of time,⁹⁾ where:

a_n is the quantity of a nuclide released from the specimen during leaching interval n , corrected for radioactive decay (see 3.2);

$\sum a_n$ is the cumulative quantity of a nuclide released from the specimen from the beginning of the first leaching interval to the end of the leaching interval of concern, corrected for radioactive decay;

A_o is the total quantity of a given contaminant in the specimen at the beginning of the first leaching interval (i.e., after the initial 30-s rinse);

$\sum(\Delta t)_n = t_n = t$ is the cumulative leaching time, since the beginning of the first leaching interval (s);

$(\Delta t)_n = t_n - t_{n-1}$ is the duration, of the n 'th leaching interval (s).

As required in 2.3, the leachate shall be replaced with fresh leachant very quickly, so that change-out time is insignificant when compared to the time of a leaching interval. Thus, for all practical purposes, "elapsed clock time," t_c , at the end of a leaching interval is equal to the sum of all the leaching intervals up to that time; that is, $t_c \cong \sum(\Delta t)_n$.

4.2 Analysis of Results

After initial rapid removal of mobile surface contamination (wash-off), the early leach rates observed with solidified waste forms are most often explained by diffusion.¹⁰⁾ If other mechanisms (e.g., corrosion, erosion, dissolution, etc.) are important, their control is generally discernible only after longer leaching [4].

If <20% of a leachable species is leached from a uniform, regularly shaped solid, its leaching behavior (if diffusion controlled) approximates that of a semi-infinite medium. In many leaching tests the isotope being followed is stable, or its half-life is sufficiently long, relative to the duration of the test, that it may be considered stable. Under these conditions the mass-transport equations permit the calculation [4] of an "effective diffusivity" by the following expression:

⁹⁾ See Part C of Annex A.

¹⁰⁾ See Annex B.

$$D = \pi \left[\frac{a_n/A_o}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T, \quad (1)$$

where:

D is the effective diffusivity (cm²/s);

V is the volume of specimen (cm³);

S is the geometric surface area of the specimen as calculated from measured dimensions (cm²);

T is the leaching time representing the "mean time" of the leaching interval (s) as follows:

$$T = \left[\frac{1}{2}(t_n^{1/2} + t_{n-1}^{1/2}) \right]^2. \quad (2)$$

The D in Eq. (1) is based on incremental (\sim differential) data.¹¹⁾ Using the incremental fraction leached has the advantage that each data point is independent; that is, any error or bias is not carried into subsequent data points (important for the initial points).¹²⁾

If more than 20% of a leachable species has been removed by the time, t , the effective diffusivity can only be calculated from a shape specific solution of the mass transport equations [5,7]. Graphs to evaluate D (diffusion control) for cylinders are available [5]. The 20% value is an approximation but is sufficiently accurate for the purposes of this standard. More precise estimates of D from the data require more complicated calculations.

Table A.1 offers a convenient tabular way to calculate D from the experimental data for several types of cylinders. Integral data are used in this method and not incremental data as in Eq. (1). This is not a disadvantage at the advanced stage of the leaching process (i.e., after >20% has been leached). To use Table A.1, the cumulative fraction leached ($F = \sum a_n/A_o$) is calculated.¹³⁾ With this value of F , the corresponding G value for the type of cylinder represented by the specimen, identified by its length-over-diameter (ℓ/d) ratio, is obtained

from Table A.1. This value is then used with the other known quantities on the right side of Eq. (3) to arrive at D , namely,

$$D = \frac{Gd^2}{t}, \quad (3)$$

where:

G is a time factor for the cylinder, dimensionless;

d is the diameter of the cylinder (cm);

t is the elapsed leaching time since the beginning of the first leaching interval (s).

As a specific example, consider a cylindrical specimen with length $\ell = 6$ cm and diameter $d = 2$ cm. After four leaching intervals (i.e., $2 + 5 + 17 + 24 = 48$ hours or 1.73×10^5 s), 50% ($F = 0.5$) of the initial amount of a nuclide is leached out by a diffusion-controlled process. The G value in the column labeled $\ell/d = 3.0$ is found to be 0.0126. This is substituted into Eq. (3) together with the other quantities to arrive at the "effective diffusivity," D_4 , from the data of the fourth leaching interval, as follows:

$$D_4 = \frac{(0.0126)(2)^2}{1.73 \times 10^5} = 2.91 \times 10^{-7} \text{ cm}^2/\text{s}.$$

In Fig. 3 a convenient graphical method is provided for evaluating D (diffusion control) for several geometries [8]. Figure 3 also serves as a vivid illustration of the significant deviation of the leaching of finite bodies from the predictions of the semi-infinite medium model, after >20% of the initial radioactivity has been leached. For various geometries, the graph gives cumulative fraction leached versus a dimensionless time factor:

$$Z = \left[(Dt) \left(\frac{S}{V} \right)^2 \right]^{1/2} \quad (4)$$

¹¹⁾ In this connection see also Annex C.

¹²⁾ All the quantities appearing on the right of Eq. (1) are required entries on the forms given in Annex A.

¹³⁾ Last column of Part C of the forms given in Annex A.

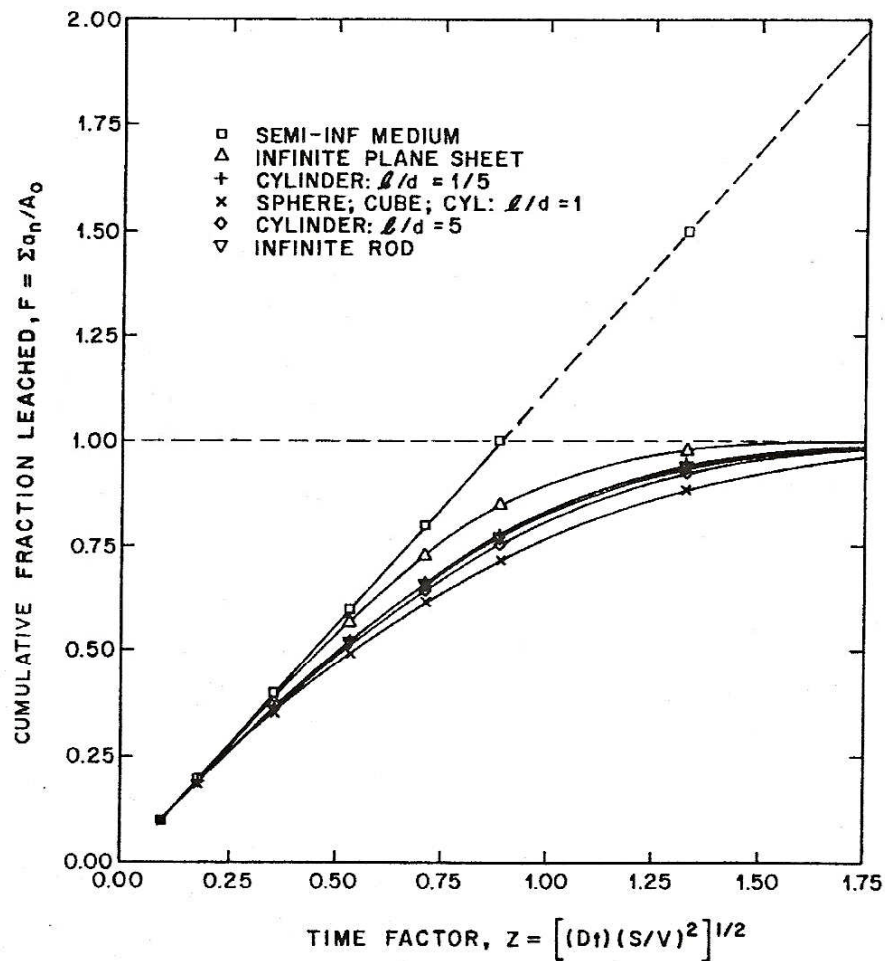


Figure 3.

with specimen geometry as a third parameter. As an illustration of the use of Fig. 3, consider the example given above for Table A.1. From the graph with a cumulative fraction leached of 0.5 and a cylinder with an ℓ/d of 3 (by interpolation between the curves for $\ell/d = 1$ and $\ell/d = 5$), the value of Z is found to be 0.52. For a specimen with the dimensions as above,

$$S = \pi d(\ell + d/2) = 43.98 \text{ cm}^2 ;$$

$$V = (\pi d^2 \ell)/4 = 18.85 \text{ cm}^3 .$$

These values along with $t = 1.73 \times 10^5$ s and $Z = 0.52$ are used in Eq. (4) to obtain D as follows:

$$Z = 0.52 = \left[D(1.73 \times 10^5) \left(\frac{43.98}{18.85} \right)^2 \right]^{1/2} ,$$

from which

$$D_4 = 2.87 \times 10^{-7} \text{ cm}^2/\text{s} ,$$

in close agreement with the value obtained above by the tabular method. For both the tabular and graphic methods, to obtain D , linear interpolation will suffice for values between those given in Table A.1 or Fig. 3.

Conversely, if a reasonable estimate of D is available, a specimen can be sized to approxi-

mate a semi-infinite medium for the time of the test using Table A.1 or Fig. 3.

In the foregoing considerations, no need to correct the data for radioactive decay was assumed; that is,

$$(a_n)_\tau = b_n \left(\frac{V_t}{v_a} \right) e^{\lambda \tau} \rightarrow b_n \left(\frac{V_t}{v_a} \right) (1) \equiv a_n, \quad (5)$$

where:

$(a_n)_\tau$ is the amount of radioactive species present in the aliquot of leachate used for analysis corrected for radioactive decay to the reference time;

b_n is the amount of radioactive species present in the aliquot of leachate used for analysis at the time of analysis;

v_a is the volume of leachate used for analysis (ml);

V_t is the volume of leachate from which v_a was taken (ml);

λ is the radioactive decay constant = $\ln 2 / t_{1/2} = 0.693 / t_{1/2}$ (s^{-1});

$t_{1/2}$ is the half-life of the radionuclide under consideration (s);

τ is the elapsed clock time from the reference time to the counting of the aliquot (s).

If the reference-source method is not used to report the data and the half-life of the radionuclide of interest is short ($t_{1/2} < 20\tau$), the counting data shall be corrected to the reference time. The beginning of the first leaching interval is frequently taken as the reference time. The correction is accomplished by multiplying b_n by its corresponding $e^{\lambda \tau}$ as shown in Eq. (5).¹⁴⁾

4.3 Determination of the Leachability Index

The Leachability Index of a nuclide, i , of concern in a material is defined as

$$L_i = \frac{1}{7} \sum_{n=1}^7 [\log(\beta/D_i)]_n, \quad (6)$$

where β is a defined constant ($1.0 \text{ cm}^2/\text{s}$) and D_i is the effective diffusivity of nuclide i calculated from the test data. These values of D_i are to be calculated by use of Eq. (1) if $\sum a_n/A_0 < 0.2$; otherwise, the tabular method and Eq. (3), or the graphical method using Fig. 3, or their equivalents for other shapes, shall be used. The mean [Eq. (6)] of the seven determinations (L_n) for each radionuclide shall be recorded as its Leachability Index (L_i). This is the single value used (in conjunction with the results of available pertaining generic studies) to classify or rank the material.

A given matrix material might have different Leachability Index values for different radionuclides if they are present as different chemical species that are more or less readily mobilized. Different Leachability Indexes for the same matrix are reported with the particular nuclide as subscript (e.g., $L_{Co}^{60} = 10.7$).

To illustrate the Leachability Index calculation, the data in Annex A, Table A.2 are used. For example 1, the mean value [Eq. (6)] of the seven $\log(\beta/D_i)_n$ values presented in Table A.2 yield

$$L_i = \frac{7.2 + 6.8 + 5.4 + 5.7 + 5.6 + 7.1 + 6.7}{7} = 6.4.$$

For example 2, the result is

$$L_i = \frac{6.4 + 6.6 + 6.1 + 5.9 + 6.1 + 6.5 + 5.6}{7} = 6.2.$$

If the "extended test" is performed, the Leaching Index is given the symbol \bar{L} and is calculated from the $\log(\beta/D_i)$ values of the first seven leaching intervals plus the added three intervals by the following expression:

$$\bar{L}_i = \frac{1}{10} \sum_{n=1}^{10} [\log(\beta/D_i)]_n. \quad (7)$$

The standard leach test is intended to serve for quantitative assessment purposes and as a ba-

¹⁴⁾ An example of this correction with Eq. (1) used to calculate D is presented in Annex C.

For the results shown in Table A.2, the confidence range (C) and the correlation coefficient (r) are calculated [Eqs. (8) and (10)] to be as follows:

Parameter	Example 1	Example 2
Standard 5-day Test		
Confidence range	4.6 to 8.1	5.4 to 7.0
Correlation coefficient	0.09	-0.65
Extended 90-day Test		
Confidence range	5.4 to 7.9	5.5 to 6.6
Correlation coefficient	0.56	-0.59

The calculations made to obtain these statistical parameters shall be carried out to at least two more significant figures than the original values of L_n and t_n . No rounding-off shall be done until the final results are obtained. The confidence interval shall be reported to one decimal position only, and the correlation coefficient to two decimal positions.

The confidence range and correlation coefficient shall be reported with the Leachability Index.

4.4 Limitations of Results

To be practicable, a standard leach test must permit accumulation of sufficient data to determine material parameters (e.g., L or \bar{L}) in a relatively short time. To be meaningful, however, these L (or \bar{L}) values must be related to long-term leaching studies carried out with similar-type materials (i.e., generic studies) under a wide range of conditions, which determine the actual mass transport mechanisms. These provide the background for interpreting the results of a short-term standard leach test.

If the only leaching mechanism occurring in the waste form is diffusion-controlled leaching, the Leachability Index (L) from the standard 5-day test has an exact theoretical interpretation. The interpretation applies for the conditions of the test for any size and shape waste form made of the material [4,5,8]. This is true

as long as the initial and boundary conditions are satisfied.¹⁶⁾

The Leachability Index, as defined in this standard (L or \bar{L}), is a material parameter. It is limited to the material for which it was determined. It is meaningful only if the specimen itself did not undergo significant changes during the leach test and if the actual waste form to which it applies does not undergo changes in its material characteristics.

The logarithmic character of the Leachability Index allows a relatively wide range of experimental error and deviation from the ideal to be tolerated without a significant effect on the index value or its intended use. This is advantageous because minor perturbations that would limit the applicability of the test and the interpretation of its results are eliminated. For example, in 3.2, two methods were given for the calculation of the effective diffusivity, D_4 , from a set of data. By one method, a value of $2.91 \times 10^{-7} \text{ cm}^2/\text{s}$ was obtained; by the other, a value of $2.87 \times 10^{-7} \text{ cm}^2/\text{s}$ was obtained. The L_n value derived from either would be 6.54. Since the Leachability Index shall be reported to one decimal position only, both methods usually arrive at the same value. When interpolation (or the less precise graphical method) is necessary to determine the value of D , there may be slight variations in the decimal value. Similarly, only a drastic change of the dominant leaching mechanism from diffusion-controlled leaching during the early part of the test will seriously affect the index value obtained. Any such observation shall be reported in the manner described in 3.3.

5 References

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¹⁶⁾ See Annex B.

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